INTERGRATED LEACHATE TREATMENT BY SEQUENCING BATCH REACTOR (SBR) AND MICRO-ZEOLITE (MZ)

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ABSTRACT

Biological treatment has a lot of potential in leachate treatment with the ability of the biodegradable substrates and this method can reduce the cost of treatment residues with respect to ecological and economical requirements.The aims of this study are to investigate the effect of biological treatment by using sequencing batch reactor (SBR) system in different condition consisting anaerobic (An), anoxic (Ax), and oxic (Ox) with different reaction time. An integration in combining phases consisting An/Ax/Ox is used in order to achieve maximum removal. Then, followed by the performance of combination phases consisting An/Ax/Ox in SBR system with addition of adsorption adsorbent micro-zeolite (MZ) (size range 75-150 µm) at different dosages. The raw leachate and sludge were collected from sanitary landfill from Tanjung Langsat, Pasir Gudang. An condition has better performance in an SBR system at optimum reaction time 11 hr promoting the percentage removal efficiency of chemical oxygen demand (COD), ammonia nitrogen (AN), total nitrogen (TN), total phosphorus (TP) and suspended solid (SS) and turbidity which were 77%, 74.65%, 75.07%, 76.05%, 63.91%, and 62.67% respectively. The result indicated that the combined condition consisting An/Ax/Ox at the optimum time reaction of each condition gives the removal efficiency COD, AN, TN, TP, SS, and turbidity which were 85.78%, 88.65%, 87.07%, 86.9%, 81.92% and 81.15% respectively. The application addition of adsorption adsorbent gives optimum dosage at 5 g/L. The addition of MZ shows good removal efficiency which were more than 90% at overall parameter.

ABSTRAK

Rawatan biologi mempunyai banyak potensi dalam rawatan larut resapan yang keupayaan mesra alam dan kaedah ini boleh mengurangkan kos sisa rawatan dengan mengambil kira keperluan ekologi dan ekonomi. Matlamat kajian ini adalah untuk mengkaji kesan rawatan biologi dengan menggunakan reaktor kelompok penjujukan (SBR) sistem dalam keadaan yang berbeza yang terdiri anaerobik (An), anosik (Ax), dan aerobik (Ox) dengan masa tindak balas yang berbeza. Gabungan fasa terdiri An/Ax/Ox dalam usaha untuk mencapai penyingkiran maksimum. Kemudian, diikuti dengan prestasi fasa gabungan yang terdiri An/Ax/Ox dengan penambahan adsorben penjerapan mikro-zeolit (MZ) (pelbagai saiz 75-150 µm) pada dos yang berlainan (1, 3, 5, 7, 9 dan 11 g/L). Larut lesapan dan enap cemar dikumpulkan dari tapak pelupusan sanitari dari Tanjung Langsat, Pasir Gudang. Semua ujian telah dijalankan di Makmal Alam Sekitar, Universiti Tun Hussein Malaysia mengikut kaedah standard (APHA 2005). Keadaan An mempunyai prestasi tertinggi pada masa tindak balas yang optima 11 jam dalam peratus penyingkiran kecekapan permintaan oksigen kimia (COD), ammonia nitrogen (AN), jumlah nitrogen (TN), jumlah fosforus (TP), pepejal terampai (SS) dan kekeruhan yang masing-masing 77%, 74.65%, 75.07%, 76.05%, 63.91%, dan 62.67%. Keputusan menunjukkan An/Ax/Ox (11/8/5jam) memberikan peratus penyingkiran kecekapan COD, AN, TN, TP, SS, dan kekeruhan yang masing-masing 85.78%, 88.65%, 87.07%, 86.9%, 81.92%, dan 81.15%. Penambahan aplikasi penjerapan bahan penjerap memberikan dos optima pada 5 g / L. Penambahan MZ menunjukkan kecekapan penyingkiran yang baik yang lebih daripada 90% pada parameter keseluruhan.

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LIST OF SYMBOL AND ABBREVIATIONS

Alum	Aluminium (III) Sulphate
AN	Ammonia nitrogen
An	Anerobic
AOB	Ammonia Oxidizing Bacteria
AOP	Advanced Oxidation Processes
Ax	Anoxic
BOD	Biological oxygen demand
CH_4	Methane gas
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DO	Dissolve Oxigen
HCl	Hydrochloric Acid
HRT	Hydraulic Retention Time
MBR	Membrane bioreactor
MF	Microfiltration
MFC	Microbial Fuel Cell
MLSS	Mixed Liquor Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solid
MSBR	Membrane Sequencing Batch Reactor
MSW	Municipal Solid Waste
MZ	Micro-zeolite
N_2	Nitrogen gas
NF	Nanofiltration

NH_3	Ammonia
NH3-N	Ammonia Nitrogen
NH_4^+	Ammonium
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
NOB	Nitrite Oxidizer Bacteria
OLR	Organic Loading Rate
ORP	Oxidation-Reduction Potential
Ox	Oxic/ aerobic
PAC	Powdered activated carbon
PACl	Polyaluminium chloride
RBC	Rotating Biological Contactor
RO	Reverse osmosis
SBR	Sequencing batch reactor
sCOD	Soluble Chemical Oxygen Demand
SRT	Sludge Retention time
SS	Suspended solid
SVI	Sludge Volume Index
TDS	Total Dissolved solid
TFE	Politetraflouroeteline
TKN	Total Kjeldahl nitrogen
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
UASB	Up-Flow Anaerobic Sludge Blanket
UF	Ultrafiltration
UV	Ultraviolet

VFA	Volatile Fatty Acid
VMPR	Volumetric Methane Production Rate
VSEPRO	Vibratory Shear-Enhanced Processing Reverse Osmosis
Å	Angstrom
µ	Micron

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CHAPTER 1

INTRODUCTION

1.1 Background on landfill leachate

The growing production of domestic and industrial wastes in the world causes serious disposal problems. An ineffectiveness of management solid waste will cause various problems of ground-water pollution and surface water, giving effect to the human health and aquatic life (Aziz *et al.*, 2010). Landfilling is one of the most widely employed methods for its management and landfill sites have been developed as highly engineered facilities designed to minimize the negative effect of the waste on the surrounding environment (Renou *et al.*, 2008; Kurniawan *et al.*, 2006).

Solid waste landfill sites are often defined as toxic and heavily polluted wastewaters with considerable variations in both composition and volumetric flow (Lopez *et al.*, 2004). Waste entering the landfill undergoes biological, chemical and physical transformations influencing factor by water fluxes. In the landfill, there are three physical phases are present, which is a solid phase (waste), liquid phase (leachate), and gas phase, which is carbon dioxide (CO_2) and methane gas (CH_4). Solid waste disposed of in landfills will go through several stages of decomposition, will eventually result in the liquid at the bottom of the landfill leachate of known.

Landfill leachate is generated as a consequence of because rainwater percolation through wastes, chemical, biological processes in waste and the inherent water content of wastes themselves (Rivas *et al.*, 2004). Leachate is formed primarily by the percolation of precipitation through open dump landfills or through the cap of the completed site. The decomposition of organic matter such as humic acid can cause the water to be yellow, brown or black (Zouboulis & Katsoyiannis, 2004).

In the 8th Malaysia Plan (2001-2005), has included waste minimization, promotion of reuse, developing a recycling oriented society and implementation of pilot project for recycling as some of its main policy goals. The 9th Malaysia Plan (2006-2010) further emphasized the continuation of reduce, reuse, recovery and recycling of waste as well as greater use of environmentally friendly products.

Due to the design of a lifetime that spans the age of landfills over the years, the generation of leachate will continue to occur even after it is closed. Site management disposal well accelerate the stabilization process and leachate management, efficient in order to avoid water pollution in underground and surface both of which will reduce the impact to the environment. Therefore, it is highly desirable management leachate main thrust in planning strategies to develop a landfill. These include control of the production of leachate to the environment (Pohland and Harper, 1987).

1.2 Problem statements

The discharge of landfill leachate may contain a large amount of organic matter (both biodegradable and non-biodegradable carbon), ammonia nitrogen, heavy metals, chlorinated organic and inorganic salts (Uygur *et al.*, 2004; Tatsi *et al.*, 2003). Although some of these pollutants can be degraded by microorganisms, the limitation of common biological processes (degradation is only a part of the COD and limited removal of bio-refractory organic pollutants) has made it difficult to meet the correlative discharge standard (Uygur *et al.*, 2004). The generated of wastewater contains colloidal solid, coloring compound, suspended solid and oil and grease.

In Malaysia, leachate pollution is a major problem that must be handled immediately. The sources of Malaysia's official statistics report that Malaysia's population is about 30.1 million people in 2014 and population projections estimate for 2020 are expected to rise to 32.4 million people. On average, each citizen in Malaysia produces 0.8 kg of solid wastes. This amount is even larger when taking into account the individuals who live in the city. The occupant of the urban areas is estimated to produce 1.5 kg of solid wastes. The statistic show waste production is increasing every year and total estimation of waste 7,772,402 tonnes per year in 2015 (10^{th} Malaysia Plan 2011-2015).

The addition of solid waste causes the several problems in this country which local streams could become polluted with toxins seeping through the ground from the landfill site. In an effort for Malaysia to achieve developed nation status towards 2020, the sustainable management of solid waste and leachate effective, treatment should be given serious attention (Daud, 2008).

Therefore, it is believed that most efficient treatment is highly required to achieve that demand. The common treatment processes for the landfill leachate to reduce or prevent pollution of the natural environment are the biological treatment with various techniques, such as sequencing batch reactors (SBR) and its modification (Guo *et al.*, 2010; Spagni *et al.*, 2009; Neczaj *et al.*, 2008; Uygur *et al.*, 2004), upflow anaerobic sludge blanket (UASB) (Ye *et al.*, 2011; Shin *et al.*, 2001; Kennedy & Lentz, 2000), membrane bioreactor (MBR) (Ahn *et al.*, 2002) and rotating biological contactor (RBC) (Dorota *et al.*, 2010).

Then, for physicochemical treatment method are adsorption using various adsorbents (activated carbon, zeolite and husk rice), precipitation, ion exchange, coagulation-flocculation, chemical and electrochemical oxidation, and reverse osmosis (Aziz *et al.*, 2013; Bashir *et al.*, 2010; Renou *et al.*, 2008).

Biological processes based upon suspended biomass (activated sludge processes) are effective for organic carbon and nutrient removal in the high degree of variation in quality and quantity such as landfill leachate (Mojiri *et al.*, 2013). There are several reasons for utilizing biological nutrient removal processes for the treatment of leachate which may be classified as environmental economist, operational benefits and the most important of these is the control of eutrophication in the effluent receiving water. Among several technologies, SBR have been demonstrated to be feasible for biological leachate treatment (USEPA, 1995). The SBR are suitable for treating wastewaters containing high nitrogen and phosphorus for small and medium size cities of high population density. SBR has the following advantages in a small scale system: flexibility in operation, low construction and maintenance cost (Dohare *et al.*, 2014; Damar *et al.*, 2012; Neczaj *et al.*, 2008; Renou *et al.*, 2008).

For many years, conventional biological treatments and physicochemical methods are considered the most appropriate technologies for manipulation and management of high-strength effluents like landfill leachate (Li *et al.*, 2009; Renou *et al.*, 2008). Physicochemical treatments can then act as a refining step for the stabilized effluent of biologically treated leachate. An adsorption using adsorbents powdered activated carbon (PAC) and powdered zeolite (PZ) were added to pre-treated of leachate (consisted of coagulation–flocculation followed by air stripping) treatment in SBR system (Kargi and Pamukoglu, 2004). He *et al.*, (2007) was study using SBR with adding PZ to treat municipal wastewater removing TN, NH_4^+-N, TP and COD.

So, it is important to determine the most appropriate treatment option as well as the optimal operating conditions required to achieve compatibility in combination treatment processes and the maximum removal of pollutants from landfill leachate. In order to deal with these issues, research is focused in finding and improving technologies such as SBR for the suitable wastewater treatment where the operation, instrumentation, control and automation of the process are a key factor and minimize the environmental impacts. There is still a need to reveal the effect of some operational parameters (reaction time and condition such as anaerobic, anoxic or aerobic) on the SBR system process. Therefore, this research which uses the SBR system attempted at investigating the influence of reaction time and examine the influence of a combination of conditions also the addition of the absorption zeolite at the treatment efficiency.

1.3 Objectives

The main aim of this research is to investigate the effect of treatment of leachate using the biological treatment method of SBR. Specifically, this study aims:-

1. To investigate the different condition consisting anaerobic (An), anoxic (Ax), and oxic (Ox) with different reaction time in order to achieve optimum removal.
2. To study the effectiveness combination method treatment of the SBR system in combination phases consisting An/Ax/Ox.
3. To determine an optimum performance combination phase consisting An/Ax/Ox in SBR system with the addition of adsorption adsorbent micro-zeolite (MZ) at different dosages.

1.4 Scope and limitation of studies

This research involves an extensive laboratory investigation that includes a study on the feasibility of using SBR, the treatment of leachate under various reaction time by using three different condition which are An, Ax and Ox, an integrated combination of conditions (An/Ax/Ox) and lastly addition of the absorption MZ at the treatment efficiency system. The scopes of this study are as follows:

a) Sample of leachate was collected from Tanjung Langsat Sanitary Landfill Site located at Pasir Gudang, Johor, Malaysia.

b) Seed sludge used for the biomass growth process was obtained from the leachate treatment pond of Sanitary Landfill Site Tanjung Langsat.

c) All tests were conducted at Environmental Laboratory, Universiti Tun Hussein Malaysia, according Standard Method (APHA 2005).

d) The operatives of the laboratory scale of SBR were performed following the order: Fill, React, Settle, Decant and Idle.

e) The reactor was filled with the leachate which was mixed with the seed sludge of microorganisms with aeration and they were mixed for several days to obtain a dense culture to start.

f) A series of operational reaction time (2, 5, 8, 11, 14 and 17 hr) was applied to the SBR system with different condition (An, Ax and Ox) to assess the optimum reaction time on the treatment of leachate.

g) An integration phases consisting An/Ax/Ox in order to achieve maximum removal.

h) Then, follow with a performance of combination phase consisting An/Ax/Ox in SBR system with the addition of adsorption adsorbent MZ (size range 75-150 µm). A series of different dosages (1, 3, 5, 7, 9, 11 and 13 g/L) to investigate the optimum dosage with combination condition on the treatment of leachate.

i) The parameters analyzed which is chemical oxygen demand (COD), ammonia nitrogen (AN), total nitrogen (TN), total phosphorus (TP) and suspended solid (SS) and turbidity.

1.5 Outline of thesis

This research is investigating the leachate treatment using SBR system operation and the effects of reaction time with different condition and a combination condition with a series of different dosages. This dissertation reports the experimental work performed to attain the proposed scientific goals and is organized in five chapters. The presents section:

i. Chapter 1 illustrates the general introduction, including a problem statement, objectives of the research, scope and limitation of studies and thesis layout.
ii. Chapter 2 presents a general literature review covering the topics of sanitary landfills, leachate characteristic, a factor that affecting leachate, leachate

treatment technology including chemical treatment and physical treatment, physicochemical, adsorption zeolite, biological treatment, anaerobic system, anoxic system, oxic system, SBR system its implementation, controlling factor, their advantages and disadvantages.

iii. Chapter 3 presents the used methodology of treating leachate using laboratory scale SBR system with several operational conditions.

iv. Chapter 4 presents the significant result and discussions of treating leachate in term of parameter removal efficiency.

v. Chapter 5 presents a general conclusion, recommendations and future works. References and appendices are attached at the end of the thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 Sanitary landfill

Landfilling is defined as placing solid and semi-solid wastes on the ground, compacting and covering it with suitable materials to isolate it from the environment. Most of the developed and developing countries (third world) today use design criteria that take into account topography, hydrogeology and site geology, along with economic, engineering and legal requirements for the construction and operation of landfill. An awareness of and necessity for effective solid waste management led to the sanitary landfill concept (Denison, 1996).

Sanitary landfill is the most general urban municipal solid waste (MSW) due to such advantages as simple disposal procedure, low cost, and landscape-restoring effect on holes from mineral workings (Aziz *et al.*, 2010). Up to 95% of the total MSW collected worldwide is disposed of in landfills (Kurniawan *et al.*, 2006). Next, solid waste is placed in landfills, solid waste will go through a process of physical, chemical and biological. The process of this change, causing decomposition of solid waste, then it will make up the liquid from the bottom of the landfill which is called leachate.

After that, the solid waste in the place at sanitary landfill, will undergo decomposition process beginning with the initial adjustment phase (aerobic) short to phase acidogenic and methanogenic which will involve a long period of time. Depending on the age of the landfill, the composition and flow rate of leachate is vary from site to site, seasonally at each site. The qualities of leachate are affected by many factors, such as waste type, age, seasonal weather variation, precipitation and composition (Renou *et al.*, 2008). There are three types of common sanitary landfills which are anaerobic landfill, semi-aerobic landfill, and aerobic landfill (Shimaoka *et al.*, 2000).

2.1.1 Anaerobic sanitary landfill

Anaerobic landfill is a placed where solid wastes are filled; in valley or digged area of plane field. Wastes are filled with water and in anaerobic condition. In Aziz *et al.*, (2010) review, anaerobic sanitary landfills are recognized by its sandwich-shape cover. Figure 2.1 has show the schematic diagram of an aerobic landfill site.

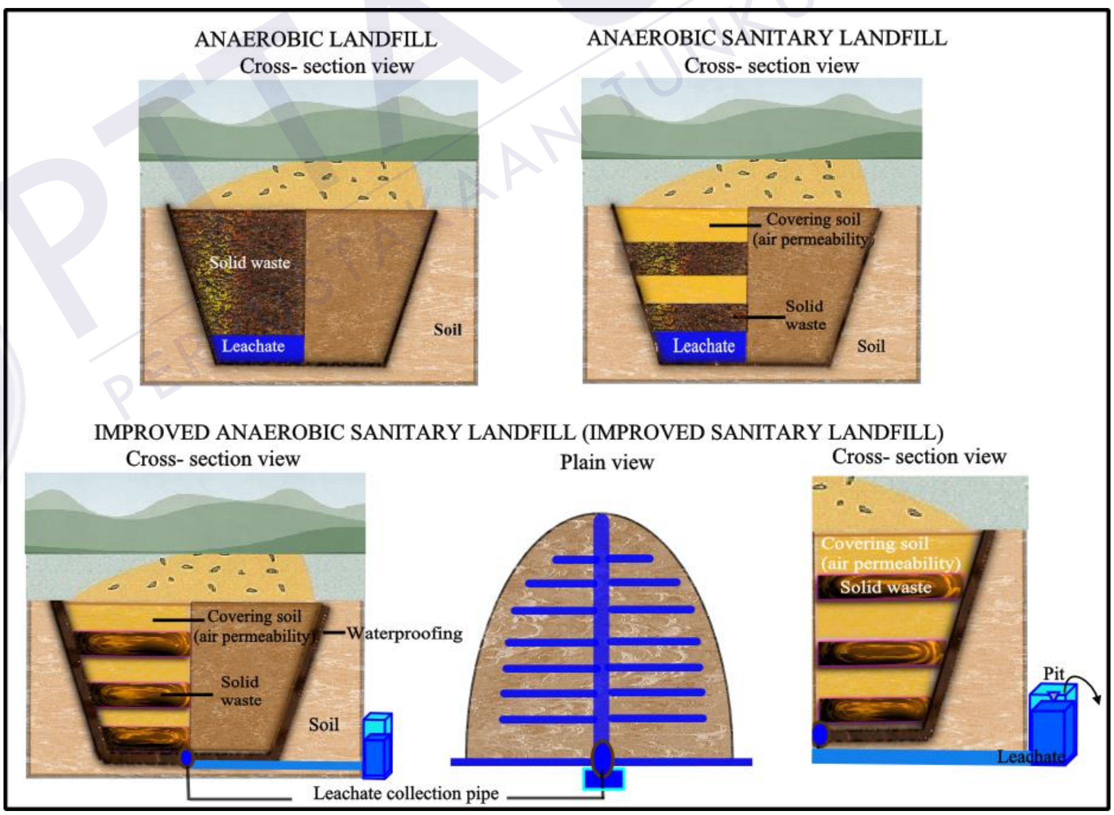

Figure 2.1: A schematic diagram of anaerobic sanitary landfill

The condition in solid waste is the same as anaerobic landfill. These disposal methods will adversely affect the environment and the community health because this system produces toxic materials and organic materials with high concentration. In addition, it also produces methane and carbon dioxide gas in large quantities that may cause global warming.

The anaerobic landfill type adverse impact on the environment and health problems in the community, because this system produce a high concentration of organic matter (Yamamoto, 2002). Then, an improved anaerobic sanitary landfill is a leachate collection system in the bottom of the landfill site. Others are same as anaerobic sanitary landfill. The conditions are still anaerobic and moisture content is much less than anaerobic sanitary landfill.

2.1.2 Semi-aerobic sanitary landfill

Semi-aerobic landfill is an attempt to lay the leachate collection pipe, including the perforated main branch pipes and gravel alongside at the bottom of the landfill to discharge leachate out of the landfill as instantaneously without delay. This prevents leachate from infiltrating into the ground water through remaining leachate draining from the bottom of the landfill. Also, oxygen in air is led into the landfill by the leachate collection pipe direct to heat convection resulting from the different temperature between the inner temperature and outside air temperature (Shimaoka *et al.*, 2000).

The leachate collection pipe of a semi-aerobic landfill has the following effects by acceleration of leachate discharge ensures lengthening aerobic atmosphere and improves activities of aerobic bacteria, leachate quality and decomposition of solid waste (Aziz *et al.*, 2010). Figure 2.2 has show the schematic diagram of semi-aerobic landfill site.

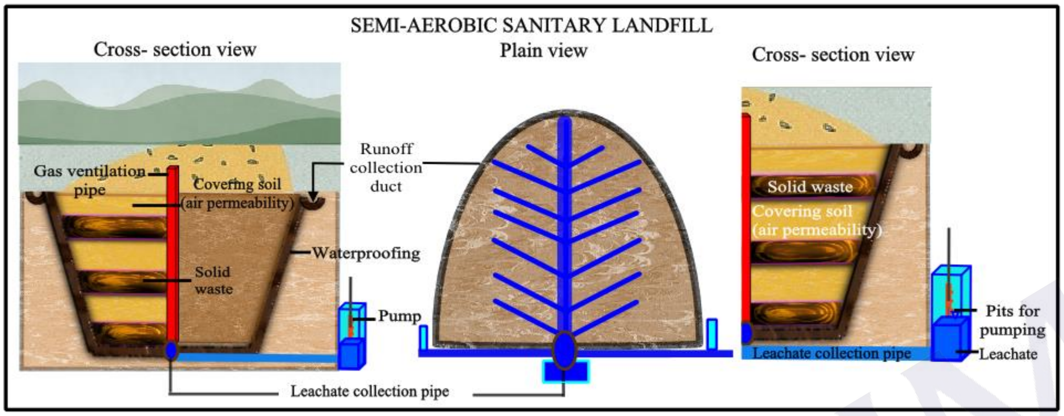

Figure 2.2: A schematic diagram of semi-aerobic sanitary landfill

2.1.3 Aerobic sanitary landfill

Aerobic landfill is designed to provide a leachate collection pipe (perforated pipes) at the bottom of the site. It is intend to collect leachate generated and then drains out of the landfill as soon as possible. In addition, it also provides ventilation pipe for supplying air into layers of solid waste and recycling leachate done. It seeks to maintain humidity and provide nutrients for the biodegradation by microorganisms (Yamamoto, 2002).

The oxygen helps to active the microorganisms then it converts the microorganisms into biodegradable waste into humus and organic matter. Figure 2.3 illustrates the schematic diagram of an aerobic landfill site.

An aerobic landfill leachate can improve quality, low producing methane gas and improve solid waste stabilization process (Huang & Zhang, 2011). Aerobic landfill leachate can also increase the decomposition process thus the stabilization process will become faster and consequently it can prolong the lifespan of the landfill site (Shimaoka *et al.*, 2000).

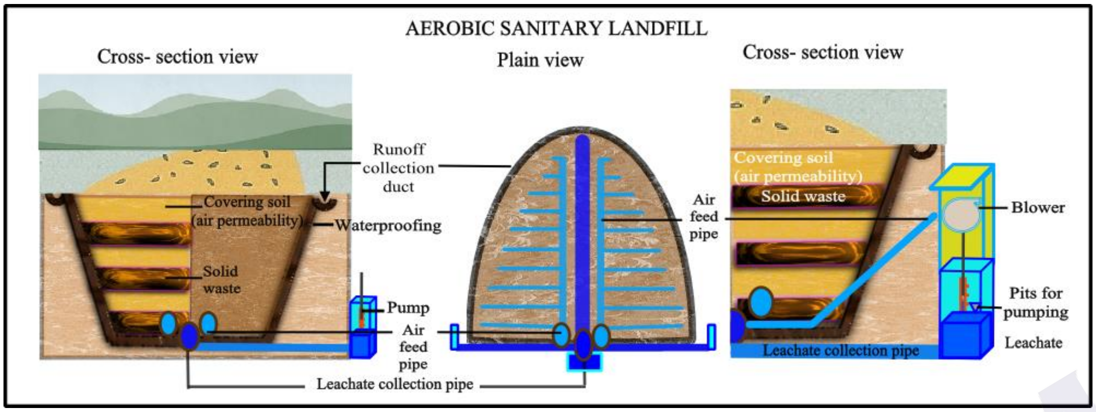

Figure 2.3: A schematic diagram of aerobic sanitary landfill

2.2 Landfills in Malaysia

In 1970, the disposal sites in Malaysia were small and the prevailing waste disposal practices were mere open dumping. This network of relatively small dumps typically was located close to population centres, and it was considered acceptable for a relatively low population of 10 million in Malaysia (Hamid & Periathamby, 2012). In the 1980s, a national programme was developed to manage municipal and industrial wastes more systematically and to decrease the adverse environmental impacts. The early 1990s saw the privatization of waste management in numerous parts of Malaysia and the establishment of the first sanitary landfills for MSW and an engineered landfill (called 'secure landfill' in Malaysia) for hazardous waste (Periathamby, 1999). Table 2.1 summarizes the classification system for new disposal sites in Malaysia.

Non-sanitary landfill in Malaysia refers to control dumps constructed without a proper engineering plan. These disposal sites were lack of the landfill bottom liner system which is needed to confine and collect leachate emissions. In the meantime, existing non-sanitary landfills are to be upgraded to Class IV landfills to minimize the pollution emissions from these dumping grounds or are required to cease operations on site-specific dates. This action has resulted in a better management and monitoring of landfills in the country (Manaf *et al.*, 2009).

Table 2.1: Classification of non-sanitary landfills in Malaysia (sources: Hamid & Periathamby, 2012)

Non-sanitary landfill class	Available facilities
I	Minimum infrastructures such as fencing and perimeter drains.
II	Class I facilities, in addition to gas removal system, separate unloading and working area, daily cover and enclosing bund (divider constructed as the embankment of different waste cells), elimination of informal scavenging and the provision of environmental protection facilities.
III	Class II facilities, in addition to leachate recirculation system allowing the collection, recirculation and monitoring of landfill leachate.
IV	Class III facilities, in addition to a leachate treatment system.

There are about 303 landfills all over the countries and 155 are operating controls dumps. The 136 of these landfills are opened dumps landfill and closed controlled. The Ministry of Housing and Local Government has selected and contracted four private waste management consortiums, each allocated a concession in a designated region of the country (Figure 2.4) (Hamid & Periathamby, 2012). Figure 2.4 depicted the coverage area of the four concessionaires of municipal solid waste management in Malaysia.

In the southern part of peninsular Malaysia, majority landfills are operated by the Southern waste Management Sdn Bhd, a concession corporation appointed by the government to handle privatization of solid waste management, whereas in the central region there is a mixture of operator between Alam Flora Sdn Bhd and local authorities (Manaf *et al.*, 2009).

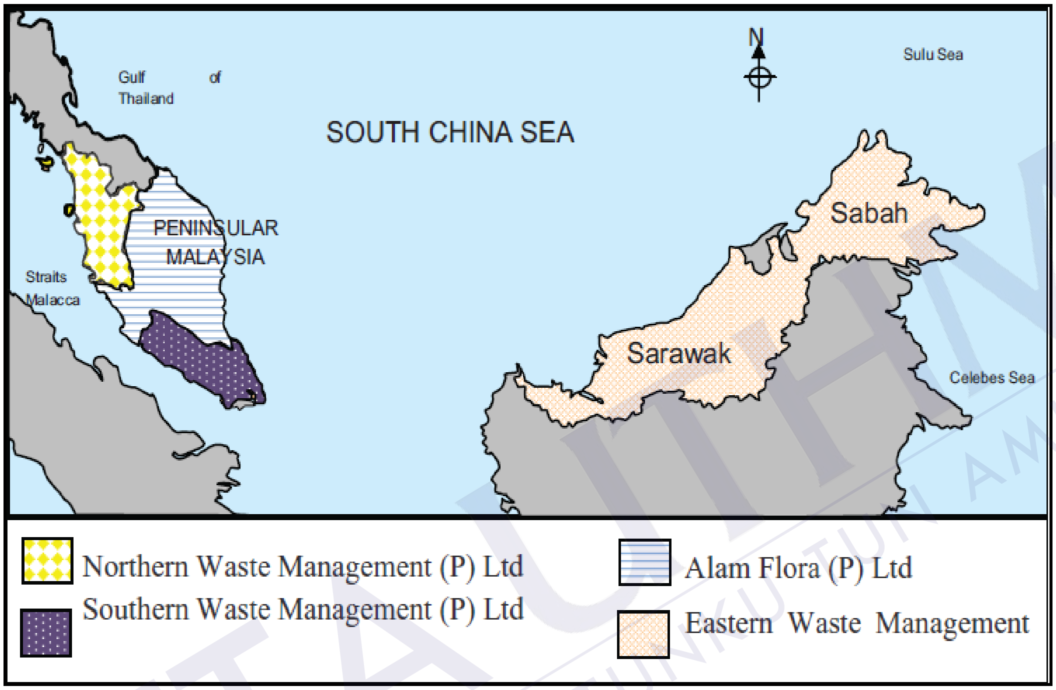

Figure 2.4: The coverage area of the four concessionaires of municipal solid waste management in Malaysia (sources: Hamid & Periathamby, 2012)

The constrained faced by with the closure of non-sanitary landfills are the difficulties in finding appropriate sites for new landfills. As a consequence, existing landfills are used continuously and temporary measures are appropriated to upgrade these landfills so as to mitigate further environmental degradation particularly leachate problem. Since the time taken to plan and construct a new landfill is approximately 2.5 years, non-sanitary landfills which are identified to be closed will be upgraded and continue to be used for the most another three years (Periathamby, 1999). Nevertheless, sanitary landfills which are safely closed can be utilized as recreational areas as well as green lungs in the future (National Solid Waste Management Department). Table 2.2 shows the sanitary landfills in Malaysia in 2010.

Table 2.2: Sanitary landfills in Malaysia in 2010 (sources: Hamid & Periathamby, 2012; Manaf *et al.*, 2009)

Name of sanitary landfill	Status of disposal facilities	In operation	Location (state)
Seelong sanitary landfill	Operating	2004	Johor
Tanjung Langsat sanitary landfill	Operating	2002	Johor
Krubong	Closed	-	Melaka
Sungai Udang	Operating	-	Melaka
Ladang Tanah Merah	Operating	-	Negeri Sembilan
Bukit Tagar sanitary landfill	Operating	2006	Selangor
Air Hitam sanitary landfill	Closed	1995	Selangor
Kg. Hang Tuah	Closed	-	Selangor
Jeram sanitary landfill	Operating	2008	Selangor
Tanjung 12 sanitary landfill	Operating	2010	Selangor
Jerangau	Operating	-	Pahang
Rimba Mas	Operating	-	Perlis
Belengu	Operating	-	Perak
Pulai	Operating	-	Kedah
Pulau Burong sanitary landfill	Operating	2001	Penang
Ampang Jajar	Operating	-	Penang
Marang	Operating	-	Terengganu
Bukit Jemalang	Operating	-	Terengganu
Mambong sanitary landfill	Operating	2000	Sarawak
Bintulu sanitary landfill	Operating	2002	Sarawak
Sibu sanitary landfill	Operating	2002	Sarawak
Miri sanitary landfill	Operating	2006	Sarawak
Kota Kinabalu sanitary landfill	Operating	2001	Sabah

Leachate quality and strength are affected by the extent of rainfall infiltration into the site, the “water balance” at the site, the nature of the waste, the rate and nature of waste degradation, the method of operation of the site, and also the measures taken for leachate management. The nature and pattern of landfill degradation processes and their effects on leachate quality are well incomprehensible (Xie *et al.*, 2012). The simplified scheme of metabolic processes in the landfill is shown in Figure 2.5.

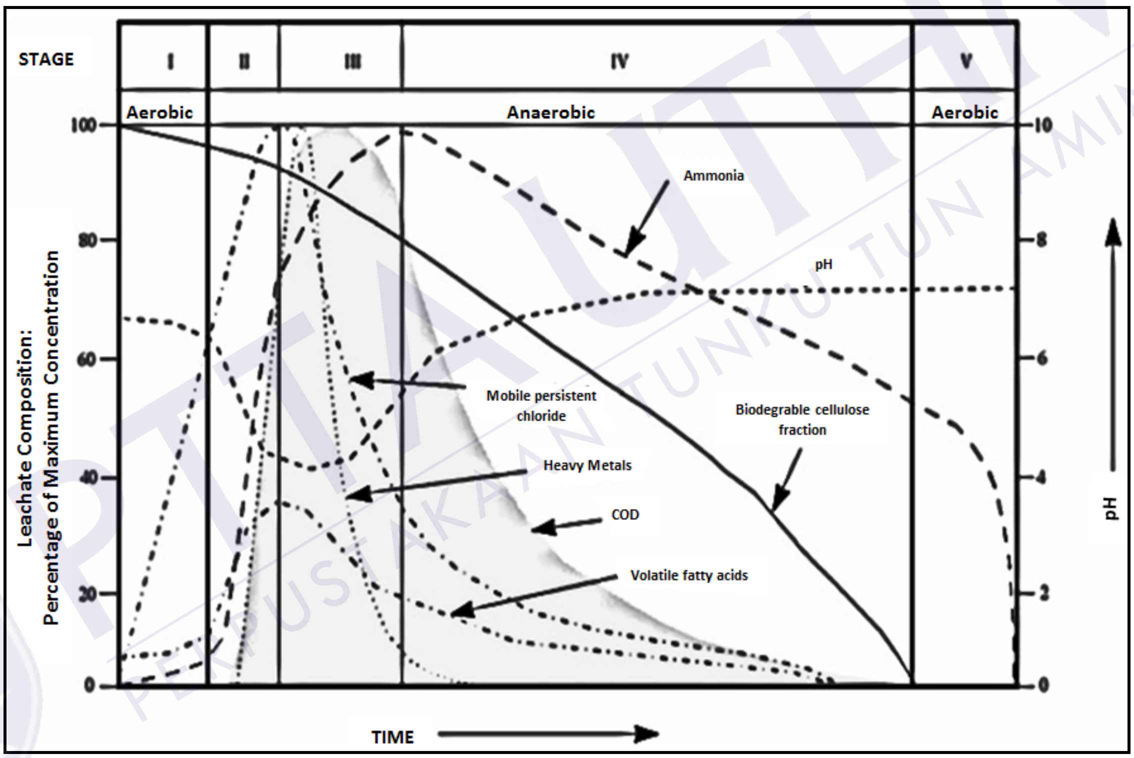

Figure 2.5: Changes in leachate composition (sources: EPA, 2000)

The principal organic content of leachate is formed during the breakdown processes at the beginning of degradation, and the quality of municipal landfill leachate changes against time as the degradation of the waste continues inside the landfill. The process is generally divided into five stages, namely (i) aerobic, (ii) hydrolysis and fermentation, (iii) acetogenesis, (iv) methanogenic and (v) aerobic phase (Peng *et al.*, 2013). The composition of landfill leachates vary greatly depending on the age of the landfill. Leachate generated at the early stages, termed as young leachate, contains a large amount of biodegradable organic matter. Then, a rapid anaerobic fermentation will take place, resulting in volatile fatty acid (VFA) as the main fermentation products (Mojiri *et al.*, 2012a).

The ratio BOD/COD leachate in this phase is high that is more than or equal to 0.5. Acid fermentation is increased by a high moisture content (water content) in the solid waste (acidogenic phase). It leads to the release of the large quantities of free VFA. As the landfill matures, the methanogenic phase occurs. Methanogenic microorganisms is developed in the waste, which increased the pH value above 7 and the VFA are converted to biogas (CH_4, CO_2) (Renou *et al.*, 2008).

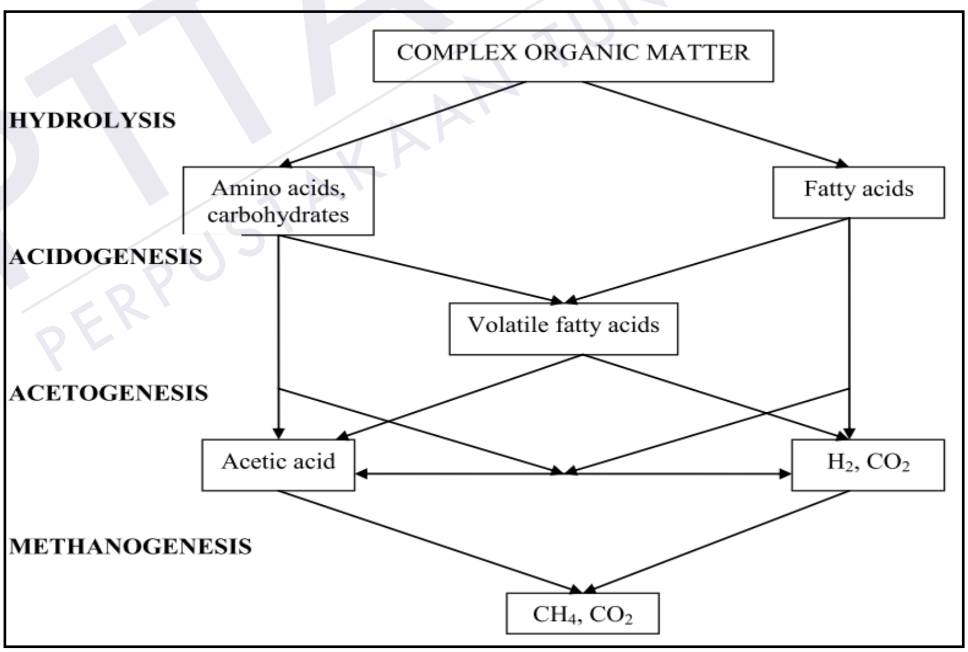

Figure 2.6: Metabolic processes in leachate (sources: Butkovskyi, 2009)

During the landfill aging, the concentration of organic compounds in leachate normally decreases and begin to be less biodegradable, whereas ammonia concentration tends to increase. As a result, leachates which is generated in the old landfills usually generate a low biochemical oxygen demand (BOD) to total Kjeldahl nitrogen (TKN) ratio (Spagni & Marsili-Libelli, 2009). After the decomposition processes, only the components that contain high molecular weight remain in the leachate. During this phase, a reduction of BOD is faster compared to the COD, causing the ratio BOD/COD ratio in leachate less than 0.1.

2.3 Leachate

Leachate which is generated from water or another liquid will subsequently react with waste, extract solutes, suspended solids or any other component of the material through which it has passed. The generation of leachate is due to principally by precipitation percolating through waste deposited in a landfill. This intimate contact allows soluble inorganic components to dissolve. Once the water and another liquid has reacted with decomposing solid waste, the percolating water will become contaminated and if it then flows out of the waste material which it is termed as leachate (Xu *et al.*, 2010).

An additional leachate volume is produced during this decomposition of carbonaceous material producing an extensive range of other materials, including methane, carbon dioxide and a complex mixture of organic acids, alcohols, aldehydes and simple sugars (Mojiri *et al.*, 2012). Figure 2.7 depicts the diagram concept illustration of a sanitary landfill site.

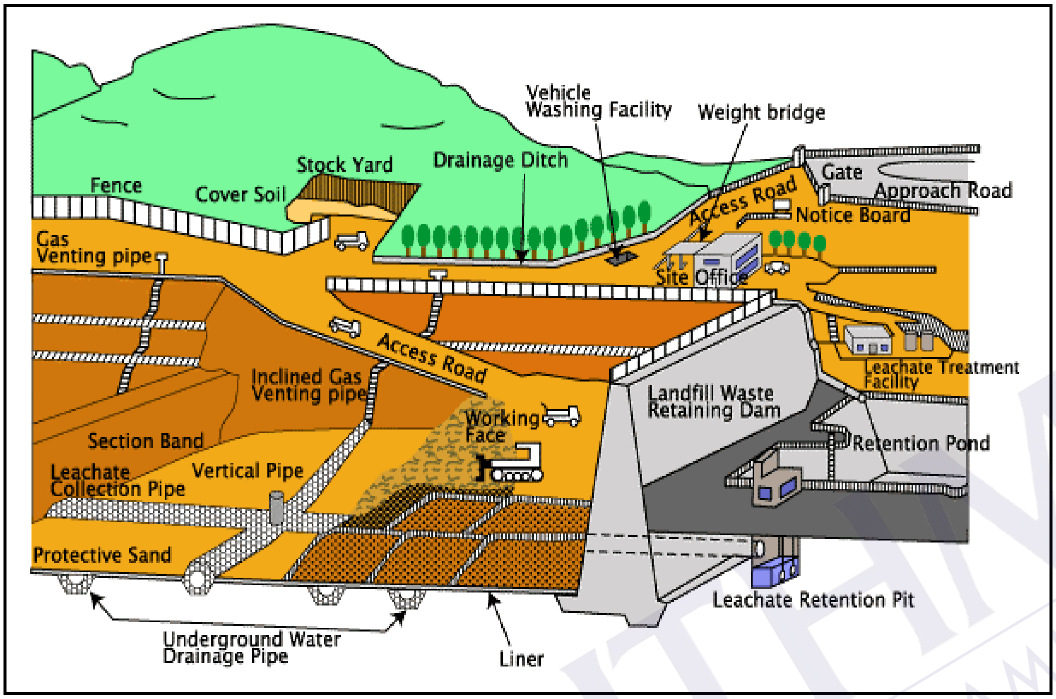

Figure 2.7: Diagram concept of sanitary landfill site (sources: Butkovskyi, 2009)

When water percolates through the waste, it favorable and assists the process of decomposition by bacteria and fungi. These processes in turn will release the by-products of decomposition and rapidly these processes using any available oxygen creating an anoxic environment. In actively decomposing waste the temperature increases and the pH falls rapidly also many of metal ions which are relatively insoluble at neutral pH may become dissolved in the developing leachate.

The processes of decomposition themselves discharge an advance water which adds to the volume of leachate. Leachate is collected by a set of collection pipes and pumps, which are installed at the bottom of a landfill (Peng *et al.*, 2013).

2.4 Composition of landfill leachate

Leachate characteristics vary considerably from one landfill to another. The main four components of leachate are (Kjeldsen *et al.*, 2002):

i. Organic matter, including dissolved organic matter, VFA, Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), COD, fulvic and humic acids.

ii. Inorganic macrocomponents: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), hydrogen carbonate (HCO_3^{-}), sulphate (SO_4^{2-}), chloride (Cl^{-}) iron (Fe^{2+}) and ammonium (NH_4^{+}).

iii. Heavy metal : nickel (Ni^{2+}), cadmium (Cd^{2+}), chromium (Cr^{3+}), lead (Pb^{2+}), zinc (Zn^{2+}) and copper (Cu^{2+})

iv. Xenobiotic organic compounds – including a huge variety of aromatic hydrocarbons, pesticides and benzene. These compounds are usually present at very low concentrations.

Generally, landfill leachates might contain very high concentrations of dissolved organic matter and inorganic macro-components. Specific organic compounds in landfill leachate are mainly the contaminants of the most concern in addressing the impact on groundwater. Most of the toxic and dangerous organic compounds are very slowly biodegraded and persisting in the environment for long period (Mojiri *et al.*, 2012).

These compounds are able to penetrate the food chain and even if they are not detectable in the receiving body, they may be present in large quantities in the higher trophic levels, owing to their bioaccumulation characteristics (Kumar & Alappat, 2005). The differences of leachate characteristics can be found in Table 2.3.

This table clearly depicts the elevated NH_3-N concentration (majority of the studies between 1000 and 3000 mg/L), reaching values up to 5500 mg/L for mature leachate. A young leachate which has low nitrogen and organic matter content that has been treated by a few researchers in the study is also shown in this table (Kalyuzhnyi & Gladchenko 2004; Tatsi *et al.*, 2003). The release of the large recalcitrant organic molecules from the solid wastes will cause low ratio of BOD_5/COD and fairly high NH_3-N of old landfill leachate.

During the acid phase in landfill sites, leachate may show low pH values and high concentrations of many compounds, in particular high concentrations of easily degradable organic compounds as volatile fatty acids. In the later stable methanogenic phase, the pH increases and the low BOD_5/COD ratio, reflecting the degradability of the organic carbon is lowered dramatically (Kjeldsen *et al.*, 2002).

Although leachate composition may vary widely within the successive aerobic, acetogenic, methanogenic, stabilization stages of the waste evolution, there are three types of leachates which have been defined according to landfill age (Table 2.4). Table 2.4 summarizes the classification of landfill leachate according to the composition changes. In this case, young acidogenic landfill leachate is commonly characterized by high COD (10,000–60,000 mg/L), >10 000 concentrations, high ratio of BOD/COD ranging from 0.4 to 0.7 and a pH value as low as 4, with biodegradable volatile fatty acids (VFAs) appear to be its major constituents (Aziz et al. 2007).

Moderately landfill has high strength of ammonia-nitrogen (500–2000 mg/L). Old landfill leachate relatively has low COD values and low ratio of BOD/COD compared to COD values of young landfills because of the decomposition processes. The concentration of organic compounds in leachate normally decreases and becomes less biodegradable, whereas ammonia concentration tends to increase.

Table 2.3: Composition of landfill leachate from previous researches

References	Landfill site	Parameter										
		pH	COD (mg/L)	BOD (mg/L)	TOC (mg/L)	NH_3-N (mg/L)	TKN (mg/L)	PO_4-P (mg/L)	Suspended solid (mg/L)	Alkalinity (mg/L)	Turbidity (NTU)	Colour (PtCo)
Timur *et al.* (1999)	Turkey	7.3-7.8	16200.0-20000.0	1075.0-11000.0	-	1120.0-2500.0	1350.0-2650.0	48.0-80.0	-	7050.0-12100.0	-	-
Kennedy *et al.* (2000)	Canada	6.9-9.0	3210.0-9190.0	-	-	-	-	-	-	-	-	-
Tatsi *et al.* (2003)	Greece	6.2	70900.0	26800.0	-	3100.0	3400.0	-	950.0	-	-	-
Aziz *et al.* (2004)	Malaysia	7.8-9.4	1533.0-3600.0	48.0-1120.0	-	-	-	-	159.0-1120.0	-	50.0-450.0	2340.0-8180.0
Kalyuzhnyi & Gladchenko (2004)	Moscow	6.0-7.5	9660.0-20560.0	-	-	780.0-1080.0	-	-	-	-	-	-
Uygur *et al.* (2004)	Turkey	8.6	10000.0	-	-	1590.0	-	90.0	-	-	-	-
Wu *et al.* (2004)	China	8.1	6500.0	500.0	4000.0	5500.0	-	-	-	650.0	-	12000.0
Klimiuk *et al.* (2006)	Bartoszyce	-	1237.0-1596.0	457.0-622.0	-	141.0-113.3	-	-	-	-	-	-
Tsilogeorgis *et al.* (2008)	Greece	8.3-8.8	1391.0-3977.0	-	-	207.0-279.0	-	5.2-13.7	-	1474.0-2848.0	98.0-154.0	-
Xu *et al.* (2010)	China	7.67	3876.0	548.0	-	1451.0	2018.0	-	-	9618.0	-	-
Mariam *et al.* (2010)	Australia	7.3	-	-	635.8	-	-	-	-	-	39.1	-
Gandhimathi *et al.* (2013)	India	7.4	16896.0	10812.0	-	-	-	-	-	10500.0	-	-

Table 2.4: Landfill leachate classification vs. age (Peng *et al.*, 2013; Renou *et al.*, 2008)

Parameter	Recent	Intermediate	Old
Age (years)	<5	5–10	>10
pH	<6.5	6.5–7.5	>7.5
COD (mg/L)	>10,000	4000–10,000	<4000
BOD_5/COD	>0.3	0.1–0.3	<0.1
Organic compounds	80% VFA	5–30% VFA+humic and fulvic acids	humic and fulvic acids
NH_3-N (mg/L)	<400	-	>400
Heavy metals	Low–medium	Medium	Low
Biodegradability	Important	Medium	Low

2.5 Factor affecting leachate quality

There are many factors influence the leachate quality including the types of wastes deposited in the landfill, moisture content, composition of wastes, particle size, the degree of compaction, the climate, the hydrology of the site, age of the fill and other site-specific conditions including landfill designs and types of liners used (Kumar & Alappat, 2005).

The nature of the waste organic fraction considerably influences the degradation of waste in the landfill and also the quality of the leachate produced. In particular, the presence of substances which are toxic to bacterial flora may slow down or inhibit biological degradation processes with consequences for the leachate. Generally, solid waste is consists of food waste, wood, textiles, glass, metal and paper. Organic matter in solid waste is produced from garbage, food waste, waste from agricultural and animal waste. Inorganic substances in a leachate are formed from the remaining ashes and debris of construction waste (Pohland and Harper, 1985).

An increase of waste paper will reduce the rate of decomposition of solid waste in landfill sites, this is because of the paper which contains high lignin, act to prevent anaerobic decomposition process occurs at a landfill site. The inorganic content of the leachate rely on the reaction between waste and leaching water as on pH and the majority of metals is released from the waste mass under acid conditions (Moy *et al.*, 2008).

2.5.1 Solid waste composition

The leachate quality is significantly affected by the composition of refuse. The nature of the waste organic fraction considerably influences the degradation of waste in the landfill and also the quality of the leachate produced. Leachate is usually more contaminated, than the conventional household wastewater that is used to be treated at the municipal wastewater treatment plants, thus it is regarded to be an industrial wastewater. It includes high concentrations of COD and nitrogen. BOD and phosphorous concentration can vary depending on the age of landfill and types of waste stored at the landfill (Puig *et al.*, 2011)

Landfill waste could be classified according to the degradability into the following groups:

i. Biodegradable (food, paper, wood, garden waste, textile)
ii. Chemically degradable (plastic)
iii. Non-degradable (stones, building materials, glass).

Several fractions could be defined among the biodegradable waste depending on the level of biodegradability:

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